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March 01, 2004

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APPLICATION NUMBER: *60/436,307*
FILING DATE: *December 23, 2002*
RELATED PCT APPLICATION NUMBER: *PCT/US03/40872*

By Authority of the
COMMISSIONER OF PATENTS AND TRADEMARKS

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PTO/SB/16 (10-01)
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U.S. Patent and Trademark Office; U.S. DEPARTMENT OF COMMERCE

PROVISIONAL APPLICATION FOR PATENT COVER SHEET

This is a request for filing a PROVISIONAL APPLICATION FOR PATENT under 37 CFR 1.53(c).

Express Mail Label No. EL 262425164US

INVENTOR(S)

Given Name (first and middle [if any])	Family Name or Surname	Residence (City and either State or Foreign Country)
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[X] Additional inventors are being named on the 1 separately numbered sheets attached hereto

TITLE OF THE INVENTION (500 characters max)

"IMPROVING ADHESION BETWEEN TEXTILE REINFORCING MATERIALS AND RUBBER"

CORRESPONDENCE ADDRESS

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ENCLOSED APPLICATION PARTS (check all that apply)

[X] Specification Number of Pages 25 including claims, Abstract

[ ] Drawing(s) Number of Sheets

[ ] Application Data Sheet. See 37 CFR 1.76

[ ] CD(s), Number

[ ] Other (specify)

METHOD OF PAYMENT OF FILING FEES FOR THIS PROVISIONAL APPLICATION FOR PATENT

[ ] Applicant claims small entity status. See 37 CFR 1.27.

[X] A check or money order is enclosed to cover the filing fees

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FILING FEE AMOUNT ($): $160.00

The invention was made by an agency of the United States Government or under a contract with an agency of the United States Government.

[X] No.

[ ] Yes, the name of the U.S. Government agency and the Government contract number are: ______

Respectfully submitted,

SIGNATURE John S. Child Jr

Date 12/23/02

TYPED or PRINTED NAME John S. Child, Jr.

REGISTRATION NO. (if appropriate) 28,833

TELEPHONE 215-563-4100

Docket Number: von Kreis.027

USE ONLY FOR FILING A PROVISIONAL APPLICATION FOR PATENT

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PROVISIONAL APPLICATION COVER SHEET
Additional Page

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Docket Number	von Kreis.027

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Number 2 of 2

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FEE TRANSMITTAL for FY 2002

Patent fees are subject to annual revision.

☐ Applicant claims small entity status. See 37 CFR 1.27

TOTAL AMOUNT OF PAYMENT ($) 160.00

Complete if Known	
Application Number	
Filing Date	
First Named Inventor	Thomas Falke
Examiner Name	
Group Art Unit	
Attorney Docket No.	von Kreis.027

METHOD OF PAYMENT (*check all that apply*)

☒ Check ☐ Credit card ☐ Money Order ☐ Other ☐ None

☒ Deposit Account:

Deposit Account Number	04-1406
Deposit Account Name	Dann Dorfman Herrell and Skillman

The Commissioner is authorized to: (*check all that apply*)

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FEE CALCULATION

1. BASIC FILING FEE

Large Entity Fee Code	Large Entity Fee ($)	Small Entity Fee Code	Small Entity Fee ($)	Fee Description	Fee Paid
101	740	201	370	Utility filing fee	
106	330	206	165	Design filing fee	
107	510	207	255	Plant filing fee	
108	740	208	370	Reissue filing fee	
114	160	214	80	Provisional filing fee	$160

SUBTOTAL (1) ($) 160.00

2. EXTRA CLAIM FEES FOR UTILITY AND REISSUE

			Extra Claims		Fee from below		Fee Paid
Total Claims		-20** =		X		=	
Independent Claims		- 3** =		X		=	
Multiple Dependent						=	

Large Entity Fee Code	Large Entity Fee ($)	Small Entity Fee Code	Small Entity Fee ($)	Fee Description
103	18	203	9	Claims in excess of 20
102	84	202	42	Independent claims in excess of 3
104	280	204	140	Multiple dependent claim, if not paid
109	84	209	42	** Reissue independent claims over original patent
110	18	210	9	** Reissue claims in excess of 20 and over original patent

SUBTOTAL (2) ($) . 0

***or number previously paid, if greater; For Reissues, see above*

FEE CALCULATION (continued)

3. ADDITIONAL FEES

Large Entity Fee Code	Large Entity Fee ($)	Small Entity Fee Code	Small Entity Fee ($)	Fee Description	Fee Paid
105	130	205	65	Surcharge - late filing fee or oath	
127	50	227	25	Surcharge - late provisional filing fee or cover sheet	
139	130	139	130	Non-English specification	
147	2,520	147	2,520	For filing a request for *ex parte* reexamination	
112	920*	112	920*	Requesting publication of SIR prior to Examiner action	
113	1,840*	113	1,840*	Requesting publication of SIR after Examiner action	
115	110	215	55	Extension for reply within first month	
116	400	216	200	Extension for reply within second month	
117	920	217	460	Extension for reply within third month	
118	1,440	218	720	Extension for reply within fourth month	
128	1,960	228	980	Extension for reply within fifth month	
119	320	219	160	Notice of Appeal	
120	320	220	160	Filing a brief in support of an appeal	
121	280	221	140	Request for oral hearing	
138	1,510	138	1,510	Petition to institute a public use proceeding	
140	110	240	55	Petition to revive - unavoidable	
141	1,280	241	640	Petition to revive - unintentional	
142	1,280	242	640	Utility issue fee (or reissue)	
143	460	243	230	Design issue fee	
144	620	244	310	Plant issue fee	
122	130	122	130	Petitions to the Commissioner	
123	50	123	50	Processing fee under 37 CFR 1.17(q)	
126	180	126	180	Submission of Information Disclosure Stmt	
581	40	581	40	Recording each patent assignment per property (times number of properties)	
146	740	246	370	Filing a submission after final rejection (37 CFR § 1.129(a))	
149	740	249	370	For each additional invention to be examined (37 CFR § 1.129(b))	
179	740	279	370	Request for Continued Examination (RCE)	
169	900	169	900	Request for expedited examination of a design application	

Other fee (specify) ________

*Reduced by Basic Filing Fee Paid

SUBTOTAL (3) ($) 0

SUBMITTED BY

				Complete (*if applicable*)	
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Improving Adhesion between Textile Reinforcing Materials and Rubber

Field of the Invention

The present invention relates to a method for improving direct adhesion between a textile reinforcing material, e. g., a polyester yarn or cord and an activated rubber. Moreover, the invention relates to a coating composition, a yarn, cord or fabric manufacturing process which is used for the method according to the invention, a textile reinforcing material obtainable by said process having increased adhesion to rubber and a reinforced rubber article having improved dynamic fatigue properties.

Background of the Invention

A tire is a highly engineered composite designed to provide safety and durability. Tires, in particular automotive tires for passenger cars or aircrafts, undergo significant dynamic and static stresses and strains in the course of ordinary service life. Performance is a major requirement in this product application due to ramifications of failure while in use. In order to obtain the necessary performance characteristics with regard to the proper functioning of a tire, structural reinforcement like Polyester dtex 1100 – 4400 is a required component of the tire composite. This reinforcement provides many functions in a tire application, in particular overall strength, dimensional stability for the tire and a mechanism to handle stress dissipation during operation (fatigue).

Currently, there is a well established set of products/processes to provide the reinforcing material used in passenger car and truck tire applications.

In order to use textile cords as reinforcing materials, the textile cords are treated with suitable adhesion promoters.

It is a particularly noteworthy fact that, for over more than 70 years, bonding fabric to rubber is still effected with an aqueous dispersion of a resorcinol formaldehyde latex (RFL), with a wide spectrum of choices of resin catalyst (usually caustic and ammonia), in situ and pre-formed resins, molar ratios of resorcinol/formaldehyde (RF), resin/latex (RL) solids ratio, and adhesion-promoting additives. The difficulty in bonding polyester fibers

to rubber is generally attributed to the presence of only hydroxyl (OH) and carboxyl (COOH) groups at the ends of the polyester molecules, while in nylon (for example) there is a relatively high frequency of amide (CONH) groups along the macromolecular chain. Therefore, this invention is primarily directed to polyester materials, and most particularly to adhesive-activated (AA) polyester fibers in cords, woven, knitted and non-woven fabrics used to reinforce conveyor belts, tires and hose.

Many adhesives and bonding systems ("dips") have been used for fabrics made from synthetic linear polyester yarns. Common systems like glycidyl ethers, phenolic condensates and blocked (or free) polyisocyanates are cost-ineffective and additionally suffer from various other disadvantages like precipitation and instability in baths in which fabrics are dipped. Usually, the fiber producers pre-treat the yarn with finish chemicals (e.g. silanes). Therefore, the resulting adhesive activated (AA) yarns provide an enhanced adhesion with a final adhesion system. This final adhesion system is most often based on RFL (Resorcinol-Formaldehyde-Latex). The adhesion surface on the cord is applied by its dipping in dispersions of RFL. Adhesion between cord and rubber is then achieved during curing with rubber.

Two examples of attempts to improve the adhesion of polyethylene terephthalate filaments to rubber are set forth in United States Patent 3,297,467 and 3,383,242. In these patents, polyethylene terephthalate filaments are treated with a spin finish which is an aqueous dispersion containing a polyglycidic ether of an acyclic hydrocarbon substituted by at least three hydroxyl groups or a diglycidic ether of an aliphatic diol, respectively, in combination with an amine curing agent and a lubricating agent. After heat treatment in order to bind the ether and amine components, the filaments or cord made therefrom can then be treated with an adhesive such as a RFL latex.

United States Patent 3,297,468 describes a similar finish except that the polyglycidic ether is of a cyclic hydrocarbon substituted with at least two hydroxyl groups.

Another example of an epoxide finish additive which may be employed to promote adhesion between a tire cord and an RFL adhesive is disclosed in United States Patent 3,803,035. The finish comprises a lubricating oil, an

antistatic agent, an emulsifier and a polyepoxide. Suitable antistatic agents include quaternary ammonium and pyridinium cationic agents.

United States Patent 3,911,422 and 3,968,304 are directed to a method of bonding polyester tire cords to rubber by use of a two-step process. In the first step, a dip is employed which comprises a low molecular weight polyallyl-glycidyl ether in an aqueous media. In the second step, a dip is employed comprised of an alkaline aqueous dispersion of a rubbery vinyl pyridine copolymer and a resinous composition reactive if exposed to heat.

Also see United States Patent 4,348,517 wherein the same epoxy ether silane is combined with the triglycidyl ether of a glycerol and a defined diglycidyl ether and is used as a fiber finish for polyester yarn.

United States Patent 3,793,425 also describes a process for improving the adhesion of polyester material to rubber. In the process, undrawn polyester yarn is coated with a composition containing an epoxy resin which is preferably buffered with an alkaline agent, such as sodium carbonate, lithium carbonate, potassium carbonate or ammonium hydroxide. The use of epoxy resins with alkaline catalysts to improve the adhesion of polyester to rubber is further disclosed in United States Patent 3,423,230 and United States Patent 3,464,878.

A process for treating chemically stabilized polyester material to improve the adhesion of the polyester to rubber is also described in United States Patent 4,751,143. As noted therein, the aging period for chemically stabilized, adhesive activated polyester material can be reduced by contacting the material before it is substantially drawn or stretched with a composition containing a defined epoxide compound catalyzed with ions of at least one of potassium, cesium, or rubidium at a pH of between about 7.5 to about 13.0. The application of finishes to the polymer surface generally produces a temporary surface condition such as lubrication or electrostatic charge dissipation which may be removed when the surface is subsequently exposed to multiple processing steps. Additionally, polyester surface modifications of the prior art employing epoxies to improve the adhesion of polyester to rubber for example, have resulted in the use of a high level of chemical pick-up. Other approaches employed in art to adjust the characteristics or properties of organic polymer surfaces include electrolytic and plasma treatments. However, these processes are costly and have

limited processing rates. The application of a strong acid or base has not been particularly effective in modifying surfaces and can penetrate beyond the surface, particularly in fiber structures, to cause strength loss. Polyisocyanates have been employed to enhance adhesion in the manufacture of polyester yarns (see United States Patent 3,549,740). These materials have been applied at relatively high concentration levels (greater than 0.5 wt.-%) and so generate obnoxious vapors, produce deposits on process rolls and bond filaments to filaments in the yarn bundle. Similar processing problems are encountered in the application of known polyester adhesives such as those based upon resorcinol-formaldehyde resins described in United States Patent 3,660,202 and United States Patent 3,318,750.

United States Patent 4,078,115 discloses an adhesive system for bonding polyester filaments to rubber in which a first coating is employed comprised of the reaction product of a polyepoxide and a quaternized copolymer of 4-vinylpyridine and an aminimide. A second coating of an RFL adhesive is also employed.

Canadian Pat. No. 652,487 discloses a two coat adhesive system. One coat is a composition comprising triallyl cyanurate, the other a composition comprising vinyl pyridine copolymer RFL. The triallyl cyanurate is polymerized prior to bonding to the cord.

United States Patent 3,318,750 also discloses a two coat system. One coat is an aqueous solution of the reaction product of an aldehyde and a composition derived from the reaction of an unsaturated aliphatic ester of cyanuric acid and resorcinol, the other being a RFL dispersion. Optionally the second component can be just the rubbery copolymer latex. The total solid coating is 2% to 7%. This coating is cured, and the cord embedded in rubber and vulcanized.

United States Patent 3,419,463 and United States Patent 3,419,464 also use a reaction product of resorcinol, triallylcyanurate and formaldehyde ("N-3") as part of their adhesive system.

The application of RFL requires considerable expenditure and costs. The Cords are for example treated at high temperatures to cure the adhesive coating which leads to the consumption of a lot of energy, furthermore an

additional process step for the production of tires is needed. In addition the high temperature treating is used to control the balance of the physical properties, such as strength, modulus and shrinkage, of the treated cord.

In order to improve the adhesion further adhesion promoters are added to the rubber in addition to the RFL.

It is known from the prior art that by using a suitable adhesion promoter in sufficient amounts in the rubber formulation adhesion of cords to the rubber can be achieved without applying RFL (direct cord/rubber adhesion). A major disadvantage of this method is the large amount of adhesion promoter needed to achieve the desired effect. As a consequence, the rubber properties are determined to a large extend by the properties of the used adhesion promoter. The large amounts of adhesion-promoters to be used constitute a significant expense factor.

Objects and Summary of the Invention

It is therefore a primary object of the present invention to provide an easily applicable and less material consuming method to achieve direct coating to a textile reinforcing fiber during the yarn processing steps. This method should render conventional dipping process as a separate manufacturing step unnecessary.

A second object of the present invention is the provision of a coating composition which, if applied to the reinforcing material, leads coating (topcoat) providing for an increased adhesion of the coated textile reinforcing material to the rubber compared to the non-coated textile reinforcing material, for instance a yarn.

A third object of the present invention is the provision of a textile reinforcing material having increased adhesion to rubber.

It is a fourth object of the present invention to provide a reinforced rubber article having improved dynamic fatigue properties.

The method according to the invention provides improved adhesion between a textile reinforcing material, e. g., the textile cord or a reinforcing member, and the rubber of a reinforced article, e. g., a tire, hose, V-belt or a conveyor belt.

Moreover, the method according to the invention leads to a reduction of production expenditure, since a pretreatment of reinforcing material such as a polyester yarn by dipping into adhesion promoters as a separate step during manufacturing, in addition to the elimination of the heat treatment step, is rendered redundant.

In a first embodiment the present invention relates to a method to achieve direct adhesion between a textile reinforcing material and an activated rubber comprising the steps of

(A) applying an adhesion-imparting composition to the surface of the textile reinforcing material;

(B) exposing the coated textile reinforcing material of step (A) to an elevated temperature;

(C) embedding the coated textile reinforcing material of step (B) into an activated rubber; and

(D) curing the reinforcing material containing rubber obtained from step (C) at a temperature and for a time sufficient to cure said rubber.

In a second embodiment the present invention relates to a coating composition comprising

(i) a resin having a solids content from about 10 to about 50 wt.-%, preferably from about 15 to about 30 wt.-%, most preferably from about 20 wt.-% obtainable by the reaction of triallyl cyanurates and resorcinol at high temperatures, then reacting the resulting product with formaldehyde and solubilizing it in aqueous ammonia; and

(ii) a latex having a solids content from about 30 to about 50 wt.-%, preferably about 35 to about 45 wt.-%, most preferably about 41 wt.-%;

wherein the weight-ratio of resin (i) to latex (ii) is from about 50/50 to about 80/20, based on the total weight of (i) and (ii).

In a third embodiment the present invention relates to a textile reinforcing material obtainable by the method according to the present invention having improved adhesion to rubber. With regard of the present invention "improved adhesion" means that the force (determined according to ASTM 2229-99) which has to be used to pull out the embedded fibers of the

rubber is in the range of at least about 5 to about 10 N, preferably about 15 to about 35 N, most preferably about 20 to about 80 N.

In a fourth embodiment the present invention relates to a reinforced rubber article having improved dynamic fatigue properties. Latter means that the strength of the cords embedded measured after 10.6 million cycles (Disc fatigue test ASTM 6588) was not less than about 60 %, preferably not less than 70 %, most preferably not less than 95 %.

In contrast to the prior art, it has been surprisingly found, that improved adhesion between conventional adhesive activated polyester materials and conventional activated rubbers has been achieved without using conventional resorcinol formaldehyde resins and conventional processes such as dipping and heat treating.

Detailed Description of the Invention

According to the present invention the textile reinforcing material is preferably selected from organic polymeric materials such as polyesters, polyamides, polycarbonates, polynitriles. The polyesters may be selected from any highly polymeric linear polyester obtained by heating one or more glycols of the series $HO(CH_2)_nOH$, wherein n is greater than 1, but does not exceed 10, with one or more dicarboxylic acid such as naphthalene dicarboxylic acid, 4,4'-diphenyl dicarboxylic acid or preferably terephthalic acid, or an ester forming derivative thereof. Examples of ester forming derivatives of dicarboxylic acids are their aliphatic (including cyclo-aliphatic) and aryl esters and half-esters, its acid halides and their ammonium and amine salts. Examples of glycols are ethylene, trimethylene, tetramethylene, hexamethylene and decamethylene glycols.

Additionally, the polyester may be reacted or blended with compatible compounds or polymers which do not substantially adversely affect the characteristics of the polyester. For example, compounds yielding non-ester linkages can be added into the reaction mixture for the polyester or pigments, fillers, anti-oxidants, etc. can be blended with the polyester. The preferred polymer for purposes of this invention will be composed of at least about 85 wt.-%, preferably about 95 wt-% polyethylene terephthalate (PET)

or polyethylene naphthalate (PEN) and will most preferably be substantially all polyethylene terephthalate or polyethylene naphthalate.

The material into which the polyester is formed can be any size and configuration amenable to processing which will undergo adhesive activation. The material can therefore be filaments, yarns, cords, fabrics, tapes or films. Preferably, the material is filaments or yarn that is melt spun and quenched, particularly those intended for adhesion to rubber as in the production of tires. Illustrative of such polyester material is multifilament polyethylene terephthalate yarn, which is highly crystalline and highly orientated.

The preparation of such high crystalline and highly orientated yarn is, for example, set forth in United States Patent 4,414,169, the disclosure of which is fully incorporated herein by reference. An alternate process for preparing multifilament polyethylene terephthalate yarn is set forth in United States Patent 4,195,052, the disclosure of which is fully incorporated herein by reference.

The polyester material used in the present invention may or may not be chemically stabilized. Under typical preparation conditions, a polyester, such as polyethylene terephthalate, has a level of carboxyl end groups ranging from about 30 to about 40 microequivalents per gram. To obtain chemical stabilization of the polyester, a compound such as ethylene carbonate, phenyl glycidyl ether, or preferably ethylene oxide, is incorporated into the polyester material. For example, ethylene oxide can be added to a polyester melt which is maintained at a pressure of from about 3,548 kPa to about 35,480 kPa in accordance with the disclosures of United States Patents 4,016,142 and 4,442,058, the disclosure of each of which is fully incorporated herein by reference.

Although the invention is described in terms of the adhesive activating of polyester material, it will be appreciated that other polymers which may be activated by the present activator systems may likewise be treated. Such polymers include polyamides, especially aromatic polyamides (e.g., Kevlar), nylon, polycarbonate, rayon and other textile reinforcing fibers.

The term "filament" or "fiber", as used herein, refers to the components which make up a yarn.

The term "yarn", as used herein, is a generic term for a continuous strand of fibers, or filaments.

The term "cord" as used herein refers to a plurality of polyester filaments or yarns twisted together to form a single string or reinforcement element. In one illustrated embodiment, the cord comprises 2 to 3 yarns, has a linear density of dtex about 2200 to about 8800, a twist multiplier of about 2.0 to 7.5 (turns per meter/√dtex).

The cord of the invention is preferably made of polyester such as polyethylene terephthalate (PET) or polyethylene naphthalate (PEN).

The polyester yarns applied in the present invention are preferably adhesive activated yarns having high-modulus-low-shrink (HMLS) properties. Such yarn having a high modulus, preferably less than about 5% elongation at a load of about 40 cN/tex. They are manufactured by high speed spinning followed by applying a finish comprising epoxy-compounds as described in GB-A-1012935, European published patent application 0420333 and United States Patent 3,775,150 or halohydroxy compounds as described in United States Patent 5,328,765, the disclosure of each of which is fully incorporated herein by reference. Afterwards the yarn is drawn and heat-treated.

(A) Application of the Topcoat

The textile reinforcing material is coated on its surface by contacting the material after it has been drawn and/or heat set with a coating composition comprising

(i) a resin obtainable by the reaction of triallyl cyanurate and resorcinol at temperatures from about 180 to about 280°C, preferably about 200 to about 260°C, most preferably about 220 to about 240°C then reacting the resulting product with formaldehyde and solubilizing it in aqueous ammonia;

(ii) a latex;

wherein the weight-ratio of resin (i) to latex (ii) is from about 50/50 to about 80/20, based on the total weight of (i) and (ii).

The coating composition can be an aqueous, a non-aqueous or an emulsion composition which comprises at least one polymerizable component. The reinforcing material is surface-treated/coated with said coating composition thus forming a top-coat which, after the removal/evaporation of the solvents leaves behind a coating on the surface of the reinforcing material which gives raise to an improved adhesion to rubbers, in particular activated rubbers.

Suitable resin components (i) are well known in the art under the designation "N-3", e.g. from United States Patent 3,318,750 and 3,419,464 and Canadian patent application 652,487, the disclosure of each of which is fully incorporated herein by reference.

The latex component (ii) of this invention should not be considered as being limited to any specific type of synthetic rubber latex, but rather to include all of those comparable diene polymer latex compositions commonly employed in the rubber fabricating industry. It is preferred however, that the latex contains at least some vinyl pyridine latex. This well-known type of latex is formed from butadiene, styrene, and vinyl pyridine monomers, in a ratio of about 50 to about 80 wt.-% of butadiene, about and about 10 to about 25 wt.-% of vinyl pyridine monomers, usually in a ratio of about 70/15/15 wt.-%.

The coating composition may further comprise a lubricant, such as butyl stearate, ethoxylated long chain alcohols, ethoxylated polysiloxanes and mixtures thereof, in amounts ranging from about 0 to about 1% by dry weight.

The coating composition may also comprise a solvent, such as water, acetone, butyl carbitol, isopropanol, ethanol and mixtures thereof. The preferred solvent is water in an amount ranging from about 1 to about 99 %, preferably about 50 to about 95 % by weight. Water is advantageously employed as the solvent for a composition used as a coating on drawn yarn.

Other components which may be present in the coating composition include tints, fluorescent brighteners, emulsifiers, antifoaming agents, antimicrobial compounds, co-catalysts, flexibilizers such as methacrylates and mixtures thereof. The total amount of solids (i.e., all constituents except solvent) in

the topcoat composition typically ranges from about 1 to about 90% by weight, preferably from about 1 to about 50% by weight.

The coating composition can be applied to the polymeric material using any suitable means which is selected primarily based on the form of the material. Exemplary means include a metered applicator, a kiss roll, spray or foam and results in a coating level with increasing preference in the order given of at least about 0.01, 0.05, 0.1 % by weight. The coating level can be – with increasing preference in the order given - up to about 3 %, 2 %, 1.5 % and 1% by weight, based on the weight of the dry coated textile reinforcing material.

Polymerizing Step (B)

After applying the coating composition to the drawn yarn or cord it is at least partially polymerized by exposing it to an elevated temperature sufficiently high to polymerize polymerizable constituents contained in the coating composition. It is preferred to expose the coated textile reinforcing material to a temperature of from about 110 to 235° C. The exposure time at lower temperatures is several minutes, at higher temperatures it is about 60 seconds or less. At least partially polymerizing means in accordance with the present Invention that at least about 5 to about 50 mol-%, preferably about 10 to about 30 mol-%, most preferably about 15 to about 25 mol-% of the monomers are linked with each other. Optionally this polymerization step can be conducted in the normal treating process.

Curing Step (C)

After at least partially polymerizing the coating composition the coated textile reinforcing material embedded into the rubber matrix resulting in an adhesion of the rubber to the reinforcing material. Therefore, the coated polymeric reinforcing material, for instance, a polyester cord/yarn is embedded in a curable rubber and the rubber is cured for about 6 to 120 min, preferably for about 6 to about 15 min., most preferred for about 6 to about 10 min. at temperatures of about 160 to about 200°C, preferably of about 160 to about 190°C, most preferred of about 170 to about 180°C.

In a preferred embodiment of the present invention the rubber employed is an activated rubber, i.e., a rubber formulation which comprises agents

known from the prior art for improving the adhesion to RFL treated cord. Specific examples for said rubber adhesion promoters are resorcinol, hexamethoxymethyl melamine (HMMA), sulfur, sulfenamides, zinc oxide, stearic acid and carbon black.

The term "rubber" as used herein refers to carbon black and/or silica filled natural and synthetic rubber systems, which can be cured so as to exhibit elastomeric properties. For the purpose of this invention the term "elastomer" is used interchangeably with the term "rubber". Representative synthetic rubbery polymers include the diene polymers. Diene polymers comprise those polymers having rubber-like properties which are prepared by polymerizing a conjugated C_4 to C_6 diolefin such as butadiene, isoprene chloroprene copolymerized with styrene, methyl styrene and acrylonitrile, the conjugated diolefin usually being present in the mixture to the extent of at least about 40 wt.-% - based on the total of polymerizable material – and preferably in major portion. The butadiene-styrene copolymers are manufactured commercially under such names as SBR 1000, SBR 1006, SBR 1500 and 1502.

Other synthetic rubbers include the "neoprene" rubbers. "Neoprene" is a generic name which is applied to polymers of chloroprene, and copolymers of chloroprene with dienes or vinyl compounds, in which the chloroprene comprises the predominant monomer. An isobutylene-isoprene copolymer "Butyl" rubber, as well as the elastomeric ethylene-propylene copolymers and terpolymers may also be used.

The term "cured" is used interchangeably with the term "vulcanized" in conjunction with the cured rubber component of this invention denotes that the rubber component to be vulcanized has been cured to a state in which the physical properties of the rubber are developed to impart elastomeric properties to the rubber generally associated with the rubber in its conventional vulcanized state.

The rubber employed may contain customary amounts of various conventional additives such as those needed to effect or accelerate vulcanization. Examples of such materials include sulfur, sulfur chloride, sulfur thiocyanate, thiuram polysulfides and other organic or inorganic polysulfides. These components are preferably employed in amounts

varying from about 0.1 to about 10 wt.-% and preferably from about 0.3 to about 3 wt.-% of rubber.

Many other materials may also be included in the rubber composition such as pigments, antioxidants and the like, all in accordance with practices well known in the art.

The following Examples are given as illustrations of the invention. It should be understood, however, that the invention is not limited to the specific details set forth in the Examples.

The following examples are presented to illustrate the invention which is not intended to be considered as being limited thereto. In the examples and throughout percentages are by weight unless otherwise indicated.

While in accordance with the patent statutes, the best mode and preferred embodiment have been set forth, the scope of the invention is not limited thereto, but rather by the scope of the attached claims.

Examples

Commercial HMLS tire yarns from KoSa were used for the Examples. Type 792 is a non-adhesive activated yarn, Type 793 is an adhesive activated (AA) (halohydroxy based) yarn and Type 748 is another adhesive activated yarn (epoxy based).

The topcoat composition (N3-L) used in the examples was

35.7 wt.-% butadiene/styrene/vinylpyridine terpolymer (Gentac 118® from Omnova Solutions Inc., Mogadore Ohio, USA);

35.7 wt.-% N-3® from FCI Technology Inc. Bessemer City, North Carolina, USA.

28.6 wt.-% Water

The yarns or cords were coated to a total level of finish on yarn, unless otherwise stated, of 1.0 wt.-% on a dry weight basis.

The coated/treated yarns or cords were heated at 229° for 60 seconds, unless otherwise stated. The rubbers used in the examples were Rubber A a non-activated rubber (without resorcinol and formaldehyde and Rubber B an activated rubber (containing resorcinol and formaldehyde).

Example 1

1440 dtex Type 792 and 793 yarns were twisted into a 2 ply cord with a twist multiplier of 6. These cords were coated and partially polymerized for 55 seconds at 235° C and then embedded in both activated and non-activated rubbers and cured at 150° C for 30 minutes. The force to pull out the cords was measured according to ASTM 2229-99, and the results set forth in Table 1.

Table 1

Yarn (PET)	Rubber	Pull-out Adhesion (N)
792 (non-AA)	A	15
792 (non-AA)	B	25
793 (AA)	A	20
793 (AA)	B	65-85

The results in table 1 demonstrate that the combination of AA-Yarn and activated Rubber B lead to a significant increase of adhesion level. The results of 792 yarn in Rubber A represent the prior art of United States Patent 3,318,750.

Only if the rubber contains an adhesion promoter and the cord contains an active finish, significant levels of adhesion could be observed in the pull-out test.

In accordance to the present invention it has been observed, that it was sufficient to use a standard topcoat (on the yarn) and small amounts of a standard adhesion system in the rubber to achieve good adhesion. The topcoat is interacting directly with the rubber and not via the RFL.

Example 2

The adhesion of the inventive system was compared to conventional RFL dipping. Fabrics (121 epdm) were prepared from Type 793 and Type 748

cords. Both the 793 and 748 fabrics were coated with the N3-L topcoat and partially polymerized prior to the fabric being embedded in activated rubber B. One length of 793 fabric was not coated, and another dipped in a standard RFL composition with a 5% dip pick-up and cured. The rubber composite was cured for 10 min. at 177°C. The peel adhesion (ASTM 4393) of these composites is set forth in Table 2.

This example shows that the cord material obtained from coated yarns has equivalent adhesion forces compared to standard RFL dipped cords. In addition, the coated samples show a significant adhesion improvement compared to the non-coated sample.

Table 2

Yarn in Fabric	Peel Adhesion Force (N)
793 (non-coated)	65-98
793 (coated)	135-152
793 (dipped)	132-178
748 (coated)	145-159

Example 3

The fabrics for Example 2 were used to build 205/60 R15 tires. The peel adhesion of sections cut from the sidewalls was measured and the results set forth in Table 3.

Table 3

Yarn in Fabric	%Rubber Coverage	Adhesion (N)
793 (non-coated)	0	38-46
793 (coated)	10	42-54
793 (dipped)	70	53-60
748 (coated)	80	72-81

Table 3 shows the in-tire adhesion performance of calendered carcass fabrics. With all activated Rubber B skim compound the cured tire shows, under equivalent curing conditions, that coated and dipped carcass sections show equivalent adhesion performance, and low adhesion values in the case of tires built with non-coated 793. Best results for rubber coverage shows in tire cord fabric manufactured with coated 748 (AA) yarn.

Testing of these tires, high speed, endurance and durability in the flexing zone showed no difference between the fabrics.

Example 4

The effect of the curing conditions on the final adhesion (pull-out force) between rubber and cord was measured using cords from Example 1, and the results set forth in Table 4. As is evident from the results, longer curing-times and higher temperatures are beneficial to achieve higher adhesion. Preferably, curing temperatures of 160-200°C are applied, the cure time may be varied between 6-120 min.

Table 4

Pull-out Adhesion (N)

Yarn	**Curing Conditions (in Rubber B)**						
	30 min @150°C	8 min @170°C	12 min @170°C	15 min @170°C	8 min @180 °C	12 min @180°C	15 min @180°C
793	34	33	53	65	44	54	55
748	45	43	73	78	70	92	86

Example 5

The topcoat was applied at various stages of the process:

A) Yarn coated and then twisted into 2-ply cord

B) Yarn twisted into a single ply, coated and twisted into a 2-ply cord

C) Cord coated

The cords were partially polymerized, embedded in rubber B and cured. The peel force of the cured rubber was measured and the results set forth in table 5.

Table 5

Application process	Yarn Type	Pull-out Adhesion (N)
A	793	30
B	793	40
C	793	62
A	748	72
B	748	30
C	748	93

The preferred method for applying the topcoat is either at the yarn or cord stage.

Example 6

1440 dtex Type 748 yarns were coated with 0.6wt.% of N3-L, and partially polymerized for 11 seconds at 220° C. The yarns were twisted into 2-ply cords at a low twist level of 250. Control cords from the same yarn were prepared at different twist levels and dipped in a standard RFL dip composition with a 5% dip pick-up and cured in a treating oven. These cord were embedded in the activated Rubber B and cured at 150° C for 30 minutes.

Visual inspection of the cords after a peel adhesion test showed excellent adhesion of the cords (visual ratings of 4.5 to 5).

The embedded cords were subjected to a dynamic fatigue test (Disc fatigue test ASTM 6588), and the strength of the cords measured after 3.6 and 10.6 million cycles. The results are set forth in Table 6 below.

Table 6

Adhesion System	**Twist level (Turns/meter)**	**Retained strength, % (Number of cycles)**	
		3.6 million	10.6 million
RFL	370	100	94
RFL	310	92	82
RFL	250	75	47
N3-L	250	95	70

This demonstrates the superior dynamic fatigue of the inventive system, and will allow lower twist levels to be used in rubber composites.

What is claimed is:

1. A method to achieve direct adhesion between a textile reinforcing material and an activated rubber comprising the steps of

   (A) applying an adhesion-imparting composition to the surface of the textile reinforcing material;

   (B) exposing the coated textile reinforcing material of step (A) to an elevated temperature;

   (C) embedding the coated textile reinforcing material of step (B) into an activated rubber; and

   (D) curing the reinforcing material containing rubber obtained from step (C) at a temperature and for a time sufficient to cure said rubber.

2. The method of claim 1 wherein the adhesion-imparting composition is an aqueous composition.

3. The method of claim 1 wherein the adhesion-imparting composition comprises at least one polymerizable component.

4. The method of claim 1 wherein the textile reinforcing material is an organic polymeric material.

5. The method of claim 4 wherein the textile reinforcing material is selected from the group of aliphatic and aromatic polyesters, polyamides, polycarbonates and rayon.

6. The method of claim 1 wherein the coated textile reinforcing material is exposed to a temperature in the range of from about 110°C to about 250°C;

7. The method of claim 1 wherein the rubber is selected from the group consisting of diene rubbers, diene/alpha-olefin rubbers, ethylene/propylene rubbers and ethylene/alpha-olefin/diene rubbers.

8. The method of claim 1 wherein the rubber is cured at a temperature of from about 140°C to 220°C, preferably from about 160°C to 200 °C, most preferably from about 170 °C to 180°C.

9. The method according to claim 1, wherein the adhesion-imparting composition comprises

   i. a resin having a solids content from about 10 to about 50 wt.-%, preferably from about 15 to about 30 wt.-%, most preferably from about 20 wt.-% obtainable by the reaction of triallyl cyanurates and resorcinol at high temperatures, then reacting the resulting product with formaldehyde and solubilizing it in aqueous ammonia; and

   ii. a latex having a solids content from about 30 to about 50 wt.-%, preferably about 35 to 45 wt.-%, most preferably about 41 wt.-%

   wherein the weight-ratio of resin (i) to latex (ii) is from about 50/50 to about 80/20, based on the total weight of (i) and (ii).

10. A treating composition for imparting adhesion to reinforcing materials said composition comprising

   i. a resin having a solids content from about 10 to about 50 wt.-%, preferably from about 15 to about 30 wt.-%, most preferably from about 20 wt.-% obtainable by the reaction of triallyl cyanurates and resorcinol at high temperatures, then reacting the resulting product with formaldehyde and solubilizing it in aqueous ammonia; and

   ii. a latex having a solids content of from about 30 to about 50 wt.-%, preferably about 35 to 45 wt.-%, most preferably about 41 wt.-%

wherein the weight-ratio of resin (i) to latex (ii) is from about 50/50 to about 80/20, based on the total weight of (i) and (ii).

11. A textile reinforcing material obtainable by a method comprising the steps of

(A) applying an adhesion-imparting composition to the surface of the textile reinforcing material; and

(B) exposing the coated textile reinforcing material of step (A) to an elevated temperature.

12. The material of claim 11 wherein the adhesion-imparting composition is an aqueous composition.

13. The material of claim 11 wherein the adhesion-imparting composition comprises at least one polymerizable component.

14. The material of claim 11 wherein the textile reinforcing material is an organic polymeric material.

15. The material of claim 14 wherein the textile reinforcing material is selected from the group of aliphatic and aromatic polyesters, polyamide, polycarbonate and rayon.

16. The material of claim 11 wherein the coated textile, reinforcing material is exposed to a temperature in the range of from about 110°C to about 250°C;

17. The material of claim 11 wherein the adhesion-imparting composition comprises

i. a resin having a solids content from about 10 to about 50 wt.-%, preferably from about 15 to about 30 wt.-%, most preferably from about 20 wt.-% obtainable by the reaction of triallyl cyanurates and resorcinol at high temperatures, then reacting the resulting product with formaldehyde and solubilizing it in aqueous ammonia; and

ii. a latex having a solids content from about 30 to about 50 wt.-%, preferably about 35 to 45 wt.-%, most preferably about 41 wt.-%

wherein the weight-ratio of resin (i) to latex (ii) is from about 50/50 to about 80/20, based on the total weight of (i) and (ii).

18. The material of claim 11 wherein the adhesive coating is present in an amount of from about 0.01 to about 3 % by weight, preferably from about 0.05 to about 2 % by weight, and most preferably from about 0.1 to about 1.5 % by weight, based on the weight of the dry coated textile reinforcing material.

19. A reinforced rubber article having improved dynamic fatigue properties obtainable by a method comprising the steps of

(A) applying an adhesion-imparting composition to the surface of the textile reinforcing material;

(B) exposing the coated textile reinforcing material of step (A) to an elevated temperature;

(C) embedding the coated textile reinforcing material of step (B) into an activated rubber; and

(D) curing the reinforcing material containing rubber obtained from step (C) at a temperature and for a time sufficient to cure said rubber.

20. The article of claim 19 wherein the adhesion-imparting composition is an aqueous composition.

21. The article of claim 19 wherein the adhesion-imparting composition comprises at least one polymerizable component.

22. The article of claim 19 wherein the textile reinforcing material is an organic polymeric material.

23. The article of claim 19 wherein the textile reinforcing material is selected from the group of aliphatic and aromatic polyesters, polyamides, polycarbonates and rayon.

24. The article of claim 19 wherein the coated textile reinforcing material is exposed to a temperature in the range of from about 110°C to about 250°C;

25. The article of claim 19 wherein the rubber is selected from the group consisting of diene rubbers, diene/alpha-olefin rubbers, ethylene/propylene rubbers and ethylene/alpha-olefin/diene rubbers.

26. The article of claim 19 wherein the rubber is cured at a temperature of from about 140°C to 220°C, preferably from about 160°C to 200 °C, most preferably from about 170 °C to 180°C.

27. The article according to claim 19, wherein the adhesion-imparting composition applied comprises

i. a resin having a solids content from about 10 to about 50 wt.-%, preferably from about 15 to about 30 wt.-%, most preferably from about 20 wt.-% obtainable by the reaction of triallyl cyanurates and resorcinol at high temperatures, then reacting the resulting product with formaldehyde and solubilizing it in aqueous ammonia; and

ii. a latex having a solids content from about 30 to about 50 wt.-%, preferably about 35 to 45 wt.-%, most preferably about 41 wt.-%

wherein the weight-ratio of resin (i) to latex (ii) is from about 50/50 to about 80/20, based on the total weight of (i) and (ii).

28. The article of claim 19 wherein the adhesive coating is present in an amount of from about 0.01 to about 3 % by weight, preferably from about 0.05 to about 2 % by weight, and most preferably from about 0.1 to about 1.5 % by weight, based on the weight of the dry coated textile reinforcing material.

Abstract

Improving Adhesion between Textile Reinforcing Materials and Rubber

The present invention relates to a method for improving direct adhesion between a textile reinforcing material and an activated rubber. Moreover, the invention relates to a coating composition, a yarn, cord or fabric manufacturing process which is used for the method according to the invention, a textile reinforcing material obtainable by said method having increased adhesion to rubber and a reinforced rubber article having improved dynamic fatigue properties.

Improving Adhesion between Textile Reinforcing Materials and Rubber

Field of the Invention

The present invention relates to a method for improving direct adhesion between a textile reinforcing material, e. g., a polyester yarn or cord and an activated rubber. Moreover, the invention relates to a coating composition, a yarn, cord or fabric manufacturing process which is used for the method according to the invention, a textile reinforcing material obtainable by said process having increased adhesion to rubber and a reinforced rubber article having improved dynamic fatigue properties.

Background of the Invention

A tire is a highly engineered composite designed to provide safety and durability. Tires, in particular automotive tires for passenger cars or aircrafts, undergo significant dynamic and static stresses and strains in the course of ordinary service life. Performance is a major requirement in this product application due to ramifications of failure while in use. In order to obtain the necessary performance characteristics with regard to the proper functioning of a tire, structural reinforcement like Polyester dtex 1100 – 4400 is a required component of the tire composite. This reinforcement provides many functions in a tire application, in particular overall strength, dimensional stability for the tire and a mechanism to handle stress dissipation during operation (fatigue).

Currently, there is a well established set of products/processes to provide the reinforcing material used in passenger car and truck tire applications.

In order to use textile cords as reinforcing materials, the textile cords are treated with suitable adhesion promoters.

It is a particularly noteworthy fact that, for over more than 70 years, bonding fabric to rubber is still effected with an aqueous dispersion of a resorcinol formaldehyde latex (RFL), with a wide spectrum of choices of resin catalyst (usually caustic and ammonia), in situ and pre-formed resins, molar ratios of resorcinol/formaldehyde (RF), resin/latex (RL) solids ratio, and adhesion-promoting additives. The difficulty in bonding polyester fibers

to rubber is generally attributed to the presence of only hydroxyl (OH) and carboxyl (COOH) groups at the ends of the polyester molecules, while in nylon (for example) there is a relatively high frequency of amide (CONH) groups along the macromolecular chain. Therefore, this invention is primarily directed to polyester materials, and most particularly to adhesive-activated (AA) polyester fibers in cords, woven, knitted and non-woven fabrics used to reinforce conveyor belts, tires and hose.

Many adhesives and bonding systems ("dips") have been used for fabrics made from synthetic linear polyester yarns. Common systems like glycidyl ethers, phenolic condensates and blocked (or free) polyisocyanates are cost-ineffective and additionally suffer from various other disadvantages like precipitation and instability in baths in which fabrics are dipped. Usually, the fiber producers pre-treat the yarn with finish chemicals (e.g. silanes). Therefore, the resulting adhesive activated (AA) yarns provide an enhanced adhesion with a final adhesion system. This final adhesion system is most often based on RFL (Resorcinol-Formaldehyde-Latex). The adhesion surface on the cord is applied by its dipping in dispersions of RFL. Adhesion between cord and rubber is then achieved during curing with rubber.

Two examples of attempts to improve the adhesion of polyethylene terephthalate filaments to rubber are set forth in United States Patent 3,297,467 and 3,383,242. In these patents, polyethylene terephthalate filaments are treated with a spin finish which is an aqueous dispersion containing a polyglycidic ether of an acyclic hydrocarbon substituted by at least three hydroxyl groups or a diglycidic ether of an aliphatic diol, respectively, in combination with an amine curing agent and a lubricating agent. After heat treatment in order to bind the ether and amine components, the filaments or cord made therefrom can then be treated with an adhesive such as a RFL latex.

United States Patent 3,297,468 describes a similar finish except that the polyglycidic ether is of a cyclic hydrocarbon substituted with at least two hydroxyl groups.

Another example of an epoxide finish additive which may be employed to promote adhesion between a tire cord and an RFL adhesive is disclosed in United States Patent 3,803,035. The finish comprises a lubricating oil, an

antistatic agent, an emulsifier and a polyepoxide. Suitable antistatic agents include quaternary ammonium and pyridinium cationic agents.

United States Patent 3,911,422 and 3,968,304 are directed to a method of bonding polyester tire cords to rubber by use of a two-step process. In the first step, a dip is employed which comprises a low molecular weight polyallyl-glycidyl ether in an aqueous media. In the second step, a dip is employed comprised of an alkaline aqueous dispersion of a rubbery vinyl pyridine copolymer and a resinous composition reactive if exposed to heat.

Also see United States Patent 4,348,517 wherein the same epoxy ether silane is combined with the triglycidyl ether of a glycerol and a defined diglycidyl ether and is used as a fiber finish for polyester yarn.

United States Patent 3,793,425 also describes a process for improving the adhesion of polyester material to rubber. In the process, undrawn polyester yarn is coated with a composition containing an epoxy resin which is preferably buffered with an alkaline agent, such as sodium carbonate, lithium carbonate, potassium carbonate or ammonium hydroxide. The use of epoxy resins with alkaline catalysts to improve the adhesion of polyester to rubber is further disclosed in United States Patent 3,423,230 and United States Patent 3,464,878.

A process for treating chemically stabilized polyester material to improve the adhesion of the polyester to rubber is also described in United States Patent 4,751,143. As noted therein, the aging period for chemically stabilized, adhesive activated polyester material can be reduced by contacting the material before it is substantially drawn or stretched with a composition containing a defined epoxide compound catalyzed with ions of at least one of potassium, cesium, or rubidium at a pH of between about 7.5 to about 13.0. The application of finishes to the polymer surface generally produces a temporary surface condition such as lubrication or electrostatic charge dissipation which may be removed when the surface is subsequently exposed to multiple processing steps. Additionally, polyester surface modifications of the prior art employing epoxies to improve the adhesion of polyester to rubber for example, have resulted in the use of a high level of chemical pick-up. Other approaches employed in art to adjust the characteristics or properties of organic polymer surfaces include electrolytic and plasma treatments. However, these processes are costly and have

limited processing rates. The application of a strong acid or base has not been particularly effective in modifying surfaces and can penetrate beyond the surface, particularly in fiber structures, to cause strength loss. Polyisocyanates have been employed to enhance adhesion in the manufacture of polyester yarns (see United States Patent 3,549,740). These materials have been applied at relatively high concentration levels (greater than 0.5 wt.-%) and so generate obnoxious vapors, produce deposits on process rolls and bond filaments to filaments in the yarn bundle. Similar processing problems are encountered in the application of known polyester adhesives such as those based upon resorcinol-formaldehyde resins described in United States Patent 3,660,202 and United States Patent 3,318,750.

United States Patent 4,078,115 discloses an adhesive system for bonding polyester filaments to rubber in which a first coating is employed comprised of the reaction product of a polyepoxide and a quaternized copolymer of 4-vinylpyridine and an aminimide. A second coating of an RFL adhesive is also employed.

Canadian Pat. No. 652,487 discloses a two coat adhesive system. One coat is a composition comprising triallyl cyanurate, the other a composition comprising vinyl pyridine copolymer RFL. The triallyl cyanurate is polymerized prior to bonding to the cord.

United States Patent 3,318,750 also discloses a two coat system. One coat is an aqueous solution of the reaction product of an aldehyde and a composition derived from the reaction of an unsaturated aliphatic ester of cyanuric acid and resorcinol, the other being a RFL dispersion. Optionally the second component can be just the rubbery copolymer latex. The total solid coating is 2% to 7%. This coating is cured, and the cord embedded in rubber and vulcanized.

United States Patent 3,419,463 and United States Patent 3,419,464 also use a reaction product of resorcinol, triallylcyanurate and formaldehyde ("N-3") as part of their adhesive system.

The application of RFL requires considerable expenditure and costs. The Cords are for example treated at high temperatures to cure the adhesive coating which leads to the consumption of a lot of energy, furthermore an

additional process step for the production of tires is needed. In addition the high temperature treating is used to control the balance of the physical properties, such as strength, modulus and shrinkage, of the treated cord.

In order to improve the adhesion further adhesion promoters are added to the rubber in addition to the RFL.

It is known from the prior art that by using a suitable adhesion promoter in sufficient amounts in the rubber formulation adhesion of cords to the rubber can be achieved without applying RFL (direct cord/rubber adhesion). A major disadvantage of this method is the large amount of adhesion promoter needed to achieve the desired effect. As a consequence, the rubber properties are determined to a large extend by the properties of the used adhesion promoter. The large amounts of adhesion-promoters to be used constitute a significant expense factor.

Objects and Summary of the Invention

It is therefore a primary object of the present invention to provide an easily applicable and less material consuming method to achieve direct coating to a textile reinforcing fiber during the yarn processing steps. This method should render conventional dipping process as a separate manufacturing step unnecessary.

A second object of the present invention is the provision of a coating composition which, if applied to the reinforcing material, leads coating (topcoat) providing for an increased adhesion of the coated textile reinforcing material to the rubber compared to the non-coated textile reinforcing material, for instance a yarn.

A third object of the present invention is the provision of a textile reinforcing material having increased adhesion to rubber.

It is a fourth object of the present invention to provide a reinforced rubber article having improved dynamic fatigue properties.

The method according to the invention provides improved adhesion between a textile reinforcing material, e. g., the textile cord or a reinforcing member, and the rubber of a reinforced article, e. g., a tire, hose, V-belt or a conveyor belt.

Moreover, the method according to the invention leads to a reduction of production expenditure, since a pretreatment of reinforcing material such as a polyester yarn by dipping into adhesion promoters as a separate step during manufacturing, in addition to the elimination of the heat treatment step, is rendered redundant.

In a first embodiment the present invention relates to a method to achieve direct adhesion between a textile reinforcing material and an activated rubber comprising the steps of

(A) applying an adhesion-imparting composition to the surface of the textile reinforcing material;

(B) exposing the coated textile reinforcing material of step (A) to an elevated temperature;

(C) embedding the coated textile reinforcing material of step (B) into an activated rubber; and

(D) curing the reinforcing material containing rubber obtained from step (C) at a temperature and for a time sufficient to cure said rubber.

In a second embodiment the present invention relates to a coating composition comprising

(i) a resin having a solids content from about 10 to about 50 wt.-%, preferably from about 15 to about 30 wt.-%, most preferably from about 20 wt.-% obtainable by the reaction of triallyl cyanurates and resorcinol at high temperatures, then reacting the resulting product with formaldehyde and solubilizing it in aqueous ammonia; and

(ii) a latex having a solids content from about 30 to about 50 wt.-%, preferably about 35 to about 45 wt.-%, most preferably about 41 wt.-%;

wherein the weight-ratio of resin (i) to latex (ii) is from about 50/50 to about 80/20, based on the total weight of (i) and (ii).

In a third embodiment the present invention relates to a textile reinforcing material obtainable by the method according to the present invention having improved adhesion to rubber. With regard of the present invention "improved adhesion" means that the force (determined according to ASTM 2229-99) which has to be used to pull out the embedded fibers of the

rubber is in the range of at least about 5 to about 10 N, preferably about 15 to about 35 N, most preferably about 20 to about 80 N.

In a fourth embodiment the present invention relates to a reinforced rubber article having improved dynamic fatigue properties. Latter means that the strength of the cords embedded measured after 10.6 million cycles (Disc fatigue test ASTM 6588) was not less than about 60 %, preferably not less than 70 %, most preferably not less than 95 %.

In contrast to the prior art, it has been surprisingly found, that improved adhesion between conventional adhesive activated polyester materials and conventional activated rubbers has been achieved without using conventional resorcinol formaldehyde resins and conventional processes such as dipping and heat treating.

Detailed Description of the Invention

According to the present invention the textile reinforcing material is preferably selected from organic polymeric materials such as polyesters, polyamides, polycarbonates, polynitriles. The polyesters may be selected from any highly polymeric linear polyester obtained by heating one or more glycols of the series $HO(CH_2)_nOH$, wherein n is greater than 1, but does not exceed 10, with one or more dicarboxylic acid such as naphthalene dicarboxylic acid, 4,4'-diphenyl dicarboxylic acid or preferably terephthalic acid, or an ester forming derivative thereof. Examples of ester forming derivatives of dicarboxylic acids are their aliphatic (including cyclo-aliphatic) and aryl esters and half-esters, its acid halides and their ammonium and amine salts. Examples of glycols are ethylene, trimethylene, tetramethylene, hexamethylene and decamethylene glycols.

Additionally, the polyester may be reacted or blended with compatible compounds or polymers which do not substantially adversely affect the characteristics of the polyester. For example, compounds yielding non-ester linkages can be added into the reaction mixture for the polyester or pigments, fillers, anti-oxidants, etc. can be blended with the polyester. The preferred polymer for purposes of this invention will be composed of at least about 85 wt.-%, preferably about 95 wt-% polyethylene terephthalate (PET)

or polyethylene naphthalate (PEN) and will most preferably be substantially all polyethylene terephthalate or polyethylene naphthalate.

The material into which the polyester is formed can be any size and configuration amenable to processing which will undergo adhesive activation. The material can therefore be filaments, yarns, cords, fabrics, tapes or films. Preferably, the material is filaments or yarn that is melt spun and quenched, particularly those intended for adhesion to rubber as in the production of tires. Illustrative of such polyester material is multifilament polyethylene terephthalate yarn, which is highly crystalline and highly orientated.

The preparation of such high crystalline and highly orientated yarn is, for example, set forth in United States Patent 4,414,169, the disclosure of which is fully incorporated herein by reference. An alternate process for preparing multifilament polyethylene terephthalate yarn is set forth in United States Patent 4,195,052, the disclosure of which is fully incorporated herein by reference.

The polyester material used in the present invention may or may not be chemically stabilized. Under typical preparation conditions, a polyester, such as polyethylene terephthalate, has a level of carboxyl end groups ranging from about 30 to about 40 microequivalents per gram. To obtain chemical stabilization of the polyester, a compound such as ethylene carbonate, phenyl glycidyl ether, or preferably ethylene oxide, is incorporated into the polyester material. For example, ethylene oxide can be added to a polyester melt which is maintained at a pressure of from about 3,548 kPa to about 35,480 kPa in accordance with the disclosures of United States Patents 4,016,142 and 4,442,058, the disclosure of each of which is fully incorporated herein by reference.

Although the invention is described in terms of the adhesive activating of polyester material, it will be appreciated that other polymers which may be activated by the present activator systems may likewise be treated. Such polymers include polyamides, especially aromatic polyamides (e.g., Kevlar), nylon, polycarbonate, rayon and other textile reinforcing fibers.

The term "filament" or "fiber", as used herein, refers to the components which make up a yarn.

The term "yarn", as used herein, is a generic term for a continuous strand of fibers, or filaments.

The term "cord" as used herein refers to a plurality of polyester filaments or yarns twisted together to form a single string or reinforcement element. In one illustrated embodiment, the cord comprises 2 to 3 yarns, has a linear density of dtex about 2200 to about 8800, a twist multiplier of about 2.0 to 7.5 (turns per meter/√dtex).

The cord of the invention is preferably made of polyester such as polyethylene terephthalate (PET) or polyethylene naphthalate (PEN).

The polyester yarns applied in the present invention are preferably adhesive activated yarns having high-modulus-low-shrink (HMLS) properties. Such yarn having a high modulus, preferably less than about 5% elongation at a load of about 40 cN/tex. They are manufactured by high speed spinning followed by applying a finish comprising epoxy-compounds as described in GB-A-1012935, European published patent application 0420333 and United States Patent 3,775,150 or halohydroxy compounds as described in United States Patent 5,328,765, the disclosure of each of which is fully incorporated herein by reference. Afterwards the yarn is drawn and heat-treated.

(A) Application of the Topcoat

The textile reinforcing material is coated on its surface by contacting the material after it has been drawn and/or heat set with a coating composition comprising

(i) a resin obtainable by the reaction of triallyl cyanurate and resorcinol at temperatures from about 180 to about 280°C, preferably about 200 to about 260°C, most preferably about 220 to about 240°C then reacting the resulting product with formaldehyde and solubilizing it in aqueous ammonia;

(ii) a latex;

wherein the weight-ratio of resin (i) to latex (ii) is from about 50/50 to about 80/20, based on the total weight of (i) and (ii).

The coating composition can be an aqueous, a non-aqueous or an emulsion composition which comprises at least one polymerizable component. The reinforcing material is surface-treated/coated with said coating composition thus forming a top-coat which, after the removal/evaporation of the solvents leaves behind a coating on the surface of the reinforcing material which gives raise to an improved adhesion to rubbers, in particular activated rubbers.

Suitable resin components (i) are well known in the art under the designation "N-3", e.g. from United States Patent 3,318,750 and 3,419,464 and Canadian patent application 652,487, the disclosure of each of which is fully incorporated herein by reference.

The latex component (ii) of this invention should not be considered as being limited to any specific type of synthetic rubber latex, but rather to include all of those comparable diene polymer latex compositions commonly employed in the rubber fabricating industry. It is preferred however, that the latex contains at least some vinyl pyridine latex. This well-known type of latex is formed from butadiene, styrene, and vinyl pyridine monomers, in a ratio of about 50 to about 80 wt.-% of butadiene, about and about 10 to about 25 wt.-% of vinyl pyridine monomers, usually in a ratio of about 70/15/15 wt.-%.

The coating composition may further comprise a lubricant, such as butyl stearate, ethoxylated long chain alcohols, ethoxylated polysiloxanes and mixtures thereof, in amounts ranging from about 0 to about 1% by dry weight.

The coating composition may also comprise a solvent, such as water, acetone, butyl carbitol, isopropanol, ethanol and mixtures thereof. The preferred solvent is water in an amount ranging from about 1 to about 99 %, preferably about 50 to about 95 % by weight. Water is advantageously employed as the solvent for a composition used as a coating on drawn yarn.

Other components which may be present in the coating composition include tints, fluorescent brighteners, emulsifiers, antifoaming agents, antimicrobial compounds, co-catalysts, flexibilizers such as methacrylates and mixtures thereof. The total amount of solids (i.e., all constituents except solvent) in

the topcoat composition typically ranges from about 1 to about 90% by weight, preferably from about 1 to about 50% by weight.

The coating composition can be applied to the polymeric material using any suitable means which is selected primarily based on the form of the material. Exemplary means include a metered applicator, a kiss roll, spray or foam and results in a coating level with increasing preference in the order given of at least about 0.01, 0.05, 0.1 % by weight. The coating level can be – with increasing preference in the order given - up to about 3 %, 2 %, 1.5 % and 1% by weight, based on the weight of the dry coated textile reinforcing material.

Polymerizing Step (B).

After applying the coating composition to the drawn yarn or cord it is at least partially polymerized by exposing it to an elevated temperature sufficiently high to polymerize polymerizable constituents contained in the coating composition. It is preferred to expose the coated textile reinforcing material to a temperature of from about 110 to 235° C. The exposure time at lower temperatures is several minutes, at higher temperatures it is about 60 seconds or less. At least partially polymerizing means in accordance with the present Invention that at least about 5 to about 50 mol-%, preferably about 10 to about 30 mol-%, most preferably about 15 to about 25 mol-% of the monomers are linked with each other. Optionally this polymerization step can be conducted in the normal treating process.

Curing Step (C)

After at least partially polymerizing the coating composition the coated textile reinforcing material embedded into the rubber matrix resulting in an adhesion of the rubber to the reinforcing material. Therefore, the coated polymeric reinforcing material, for instance, a polyester cord/yarn is embedded in a curable rubber and the rubber is cured for about 6 to 120 min, preferably for about 6 to about 15 min., most preferred for about 6 to about 10 min. at temperatures of about 160 to about 200°C, preferably of about 160 to about 190°C, most preferred of about 170 to about 180°C.

In a preferred embodiment of the present invention the rubber employed is an activated rubber, i.e., a rubber formulation which comprises agents

known from the prior art for improving the adhesion to RFL treated cord. Specific examples for said rubber adhesion promoters are resorcinol, hexamethoxymethyl melamine (HMMA), sulfur, sulfenamides, zinc oxide, stearic acid and carbon black.

The term "rubber" as used herein refers to carbon black and/or silica filled natural and synthetic rubber systems, which can be cured so as to exhibit elastomeric properties. For the purpose of this invention the term "elastomer" is used interchangeably with the term "rubber". Representative synthetic rubbery polymers include the diene polymers. Diene polymers comprise those polymers having rubber-like properties which are prepared by polymerizing a conjugated C_4 to C_6 diolefin such as butadiene, isoprene chloroprene copolymerized with styrene, methyl styrene and acrylonitrile, the conjugated diolefin usually being present in the mixture to the extent of at least about 40 wt.-% - based on the total of polymerizable material – and preferably in major portion. The butadiene-styrene copolymers are manufactured commercially under such names as SBR 1000, SBR 1006, SBR 1500 and 1502.

Other synthetic rubbers include the "neoprene" rubbers. "Neoprene" is a generic name which is applied to polymers of chloroprene, and copolymers of chloroprene with dienes or vinyl compounds, in which the chloroprene comprises the predominant monomer. An isobutylene-isoprene copolymer "Butyl" rubber, as well as the elastomeric ethylene-propylene copolymers and terpolymers may also be used.

The term "cured" is used interchangeably with the term "vulcanized" in conjunction with the cured rubber component of this invention denotes that the rubber component to be vulcanized has been cured to a state in which the physical properties of the rubber are developed to impart elastomeric properties to the rubber generally associated with the rubber in its conventional vulcanized state.

The rubber employed may contain customary amounts of various conventional additives such as those needed to effect or accelerate vulcanization. Examples of such materials include sulfur, sulfur chloride, sulfur thiocyanate, thiuram polysulfides and other organic or inorganic polysulfides. These components are preferably employed in amounts

varying from about 0.1 to about 10 wt.-% and preferably from about 0.3 to about 3 wt.-% of rubber.

Many other materials may also be included in the rubber composition such as pigments, antioxidants and the like, all in accordance with practices well known in the art.

The following Examples are given as illustrations of the invention. It should be understood, however, that the invention is not limited to the specific details set forth in the Examples.

The following examples are presented to illustrate the invention which is not intended to be considered as being limited thereto. In the examples and throughout percentages are by weight unless otherwise indicated.

While in accordance with the patent statutes, the best mode and preferred embodiment have been set forth, the scope of the invention is not limited thereto, but rather by the scope of the attached claims.

Examples

Commercial HMLS tire yarns from KoSa were used for the Examples. Type 792 is a non-adhesive activated yarn, Type 793 is an adhesive activated (AA) (halohydroxy based) yarn and Type 748 is another adhesive activated yarn (epoxy based).

The topcoat composition (N3-L) used in the examples was

35.7 wt.-% butadiene/styrene/vinylpyridine terpolymer (Gentac 118® from Omnova Solutions Inc., Mogadore Ohio, USA);

35.7 wt.-% N-3® from FCI Technology Inc. Bessemer City, North Carolina, USA.

28.6 wt.-% Water

The yarns or cords were coated to a total level of finish on yarn, unless otherwise stated, of 1.0 wt.-% on a dry weight basis.

The coated/treated yarns or cords were heated at 229° for 60 seconds, unless otherwise stated. The rubbers used in the examples were Rubber A a non-activated rubber (without resorcinol and formaldehyde and Rubber B an activated rubber (containing resorcinol and formaldehyde).

Example 1

1440 dtex Type 792 and 793 yarns were twisted into a 2 ply cord with a twist multiplier of 6. These cords were coated and partially polymerized for 55 seconds at 235° C and then embedded in both activated and non-activated rubbers and cured at 150° C for 30 minutes. The force to pull out the cords was measured according to ASTM 2229-99, and the results set forth in Table 1.

Table 1

Yarn (PET)	Rubber	Pull-out Adhesion (N)
792 (non-AA)	A	15
792 (non-AA)	B	25
793 (AA)	A	20
793 (AA)	B	65-85

The results in table 1 demonstrate that the combination of AA-Yarn and activated Rubber B lead to a significant increase of adhesion level. The results of 792 yarn in Rubber A represent the prior art of United States Patent 3,318,750.

Only if the rubber contains an adhesion promoter and the cord contains an active finish, significant levels of adhesion could be observed in the pull-out test.

In accordance to the present invention it has been observed, that it was sufficient to use a standard topcoat (on the yarn) and small amounts of a standard adhesion system in the rubber to achieve good adhesion. The topcoat is interacting directly with the rubber and not via the RFL.

Example 2

The adhesion of the inventive system was compared to conventional RFL dipping. Fabrics (121 epdm) were prepared from Type 793 and Type 748

cords. Both the 793 and 748 fabrics were coated with the N3-L topcoat and partially polymerized prior to the fabric being embedded in activated rubber B. One length of 793 fabric was not coated, and another dipped in a standard RFL composition with a 5% dip pick-up and cured. The rubber composite was cured for 10 min. at 177°C. The peel adhesion (ASTM 4393) of these composites is set forth in Table 2.

This example shows that the cord material obtained from coated yarns has equivalent adhesion forces compared to standard RFL dipped cords. In addition, the coated samples show a significant adhesion improvement compared to the non-coated sample.

Table 2

Yarn in Fabric	Peel Adhesion Force (N)
793 (non-coated)	65-98
793 (coated)	135-152
793 (dipped)	132-178
748 (coated)	145-159

Example 3

The fabrics for Example 2 were used to build 205/60 R15 tires. The peel adhesion of sections cut from the sidewalls was measured and the results set forth in Table 3.

Table 3

Yarn in Fabric	%Rubber Coverage	Adhesion (N)
793 (non-coated)	0	38-46
793 (coated)	10	42-54
793 (dipped)	70	53-60
748 (coated)	80	72-81

Table 3 shows the in-tire adhesion performance of calendered carcass fabrics. With all activated Rubber B skim compound the cured tire shows, under equivalent curing conditions, that coated and dipped carcass sections show equivalent adhesion performance, and low adhesion values in the case of tires built with non-coated 793. Best results for rubber coverage shows in tire cord fabric manufactured with coated 748 (AA) yarn.

Testing of these tires, high speed, endurance and durability in the flexing zone showed no difference between the fabrics.

Example 4

The effect of the curing conditions on the final adhesion (pull-out force) between rubber and cord was measured using cords from Example 1, and the results set forth in Table 4. As is evident from the results, longer curing-times and higher temperatures are beneficial to achieve higher adhesion. Preferably, curing temperatures of 160-200°C are applied, the cure time may be varied between 6-120 min.

Table 4

Pull-out Adhesion (N)

Yarn	**Curing Conditions (in Rubber B)**						
	30 min @150°C	8 min @170°C	12 min @170°C	15 min @170°C	8 min @180 °C	12 min @180°C	15 min @180°C
793	34	33	53	65	44	54	55
748	45	43	73	78	70	92	86

Example 5

The topcoat was applied at various stages of the process:

A) Yarn coated and then twisted into 2-ply cord

B) Yarn twisted into a single ply, coated and twisted into a 2-ply cord

C) Cord coated

The cords were partially polymerized, embedded in rubber B and cured. The peel force of the cured rubber was measured and the results set forth in table 5.

Table 5

Application process	Yarn Type	Pull-out Adhesion (N)
A	793	30
B	793	40
C	793	62
A	748	72
B	748	30
C	748	93

The preferred method for applying the topcoat is either at the yarn or cord stage.

Example 6

1440 dtex Type 748 yarns were coated with 0.6wt.% of N3-L, and partially polymerized for 11 seconds at 220° C. The yarns were twisted into 2-ply cords at a low twist level of 250. Control cords from the same yarn were prepared at different twist levels and dipped in a standard RFL dip composition with a 5% dip pick-up and cured in a treating oven. These cord were embedded in the activated Rubber B and cured at 150° C for 30 minutes.

Visual inspection of the cords after a peel adhesion test showed excellent adhesion of the cords (visual ratings of 4.5 to 5).

The embedded cords were subjected to a dynamic fatigue test (Disc fatigue test ASTM 6588), and the strength of the cords measured after 3.6 and 10.6 million cycles. The results are set forth in Table 6 below.

Table 6

Adhesion System	**Twist level (Turns/meter)**	**Retained strength, % (Number of cycles)**	
		3.6 million	10.6 million
RFL	370	100	94
RFL	310	92	82
RFL	250	75	47
N3-L	250	95	70

This demonstrates the superior dynamic fatigue of the inventive system, and will allow lower twist levels to be used in rubber composites.

What is claimed is:

1. A method to achieve direct adhesion between a textile reinforcing material and an activated rubber comprising the steps of

   (A) applying an adhesion-imparting composition to the surface of the textile reinforcing material;

   (B) exposing the coated textile reinforcing material of step (A) to an elevated temperature;

   (C) embedding the coated textile reinforcing material of step (B) into an activated rubber; and

   (D) curing the reinforcing material containing rubber obtained from step (C) at a temperature and for a time sufficient to cure said rubber.

2. The method of claim 1 wherein the adhesion-imparting composition is an aqueous composition.

3. The method of claim 1 wherein the adhesion-imparting composition comprises at least one polymerizable component.

4. The method of claim 1 wherein the textile reinforcing material is an organic polymeric material.

5. The method of claim 4 wherein the textile reinforcing material is selected from the group of aliphatic and aromatic polyesters, polyamides, polycarbonates and rayon.

6. The method of claim 1 wherein the coated textile reinforcing material is exposed to a temperature in the range of from about 110°C to about 250°C;

7. The method of claim 1 wherein the rubber is selected from the group consisting of diene rubbers, diene/alpha-olefin rubbers, ethylene/propylene rubbers and ethylene/alpha-olefin/diene rubbers.

8. The method of claim 1 wherein the rubber is cured at a temperature of from about 140°C to 220°C, preferably from about 160°C to 200 °C, most preferably from about 170 °C to 180°C.

9. The method according to claim 1, wherein the adhesion-imparting composition comprises

   i. a resin having a solids content from about 10 to about 50 wt.-%, preferably from about 15 to about 30 wt.-%, most preferably from about 20 wt.-% obtainable by the reaction of triallyl cyanurates and resorcinol at high temperatures, then reacting the resulting product with formaldehyde and solubilizing it in aqueous ammonia; and

   ii. a latex having a solids content from about 30 to about 50 wt.-%, preferably about 35 to 45 wt.-%, most preferably about 41 wt.-%

   wherein the weight-ratio of resin (i) to latex (ii) is from about 50/50 to about 80/20, based on the total weight of (i) and (ii).

10. A treating composition for imparting adhesion to reinforcing materials said composition comprising

   i. a resin having a solids content from about 10 to about 50 wt.-%, preferably from about 15 to about 30 wt.-%, most preferably from about 20 wt.-% obtainable by the reaction of triallyl cyanurates and resorcinol at high temperatures, then reacting the resulting product with formaldehyde and solubilizing it in aqueous ammonia; and

   ii. a latex having a solids content of from about 30 to about 50 wt.-%, preferably about 35 to 45 wt.-%, most preferably about 41 wt.-%

wherein the weight-ratio of resin (i) to latex (ii) is from about 50/50 to about 80/20, based on the total weight of (i) and (ii).

11. A textile reinforcing material obtainable by a method comprising the steps of

(A) applying an adhesion-imparting composition to the surface of the textile reinforcing material; and

(B) exposing the coated textile reinforcing material of step (A) to an elevated temperature.

12. The material of claim 11 wherein the adhesion-imparting composition is an aqueous composition.

13. The material of claim 11 wherein the adhesion-imparting composition comprises at least one polymerizable component.

14. The material of claim 11 wherein the textile reinforcing material is an organic polymeric material.

15. The material of claim 14 wherein the textile reinforcing material is selected from the group of aliphatic and aromatic polyesters, polyamide, polycarbonate and rayon.

16. The material of claim 11 wherein the coated textile reinforcing material is exposed to a temperature in the range of from about 110°C to about 250°C;

17. The material of claim 11 wherein the adhesion-imparting composition comprises

i. a resin having a solids content from about 10 to about 50 wt.-%, preferably from about 15 to about 30 wt.-%, most preferably from about 20 wt.-% obtainable by the reaction of triallyl cyanurates and resorcinol at high temperatures, then reacting the resulting product with formaldehyde and solubilizing it in aqueous ammonia; and

ii. a latex having a solids content from about 30 to about 50 wt.-%, preferably about 35 to 45 wt.-%, most preferably about 41 wt.-%

wherein the weight-ratio of resin (i) to latex (ii) is from about 50/50 to about 80/20, based on the total weight of (i) and (ii).

18. The material of claim 11 wherein the adhesive coating is present in an amount of from about 0.01 to about 3 % by weight, preferably from about 0.05 to about 2 % by weight, and most preferably from about 0.1 to about 1.5 % by weight, based on the weight of the dry coated textile reinforcing material.

19. A reinforced rubber article having improved dynamic fatigue properties obtainable by a method comprising the steps of

(A) applying an adhesion-imparting composition to the surface of the textile reinforcing material;

(B) exposing the coated textile reinforcing material of step (A) to an elevated temperature;

(C) embedding the coated textile reinforcing material of step (B) into an activated rubber; and

(D) curing the reinforcing material containing rubber obtained from step (C) at a temperature and for a time sufficient to cure said rubber.

20. The article of claim 19 wherein the adhesion-imparting composition is an aqueous composition.

21. The article of claim 19 wherein the adhesion-imparting composition comprises at least one polymerizable component.

22. The article of claim 19 wherein the textile reinforcing material is an organic polymeric material.

23. The article of claim 19 wherein the textile reinforcing material is selected from the group of aliphatic and aromatic polyesters, polyamides, polycarbonates and rayon.

24. The article of claim 19 wherein the coated textile reinforcing material is exposed to a temperature in the range of from about 110°C to about 250°C;

25. The article of claim 19 wherein the rubber is selected from the group consisting of diene rubbers, diene/alpha-olefin rubbers, ethylene/propylene rubbers and ethylene/alpha-olefin/diene rubbers.

26. The article of claim 19 wherein the rubber is cured at a temperature of from about 140°C to 220°C, preferably from about 160°C to 200 °C, most preferably from about 170 °C to 180°C.

27. The article according to claim 19, wherein the adhesion-imparting composition applied comprises

   i. a resin having a solids content from about 10 to about 50 wt.-%, preferably from about 15 to about 30 wt.-%, most preferably from about 20 wt.-% obtainable by the reaction of triallyl cyanurates and resorcinol at high temperatures, then reacting the resulting product with formaldehyde and solubilizing it in aqueous ammonia; and

ii. a latex having a solids content from about 30 to about 50 wt.-%, preferably about 35 to 45 wt.-%, most preferably about 41 wt.-%

wherein the weight-ratio of resin (i) to latex (ii) is from about 50/50 to about 80/20, based on the total weight of (i) and (ii).

28. The article of claim 19 wherein the adhesive coating is present in an amount of from about 0.01 to about 3 % by weight, preferably from about 0.05 to about 2 % by weight, and most preferably from about 0.1 to about 1.5 % by weight, based on the weight of the dry coated textile reinforcing material.

Abstract

Improving Adhesion between Textile Reinforcing Materials and Rubber

The present invention relates to a method for improving direct adhesion between a textile reinforcing material and an activated rubber. Moreover, the invention relates to a coating composition, a yarn, cord or fabric manufacturing process which is used for the method according to the invention, a textile reinforcing material obtainable by said method having increased adhesion to rubber and a reinforced rubber article having improved dynamic fatigue properties.